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Dielectric and conductivity properties of some amides in solid polymer matrices

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Abstract : Dielectric and conductivity properties of some amides have been studied in a polystyrene matrix. Dielectric absorption studies have been made for benzamide. The measurements exhibited a single absorption peak, which was identified as due to the molecular relaxation process. AC conductivity being associated with dielectric dispersion, has also been evaluated for three amides namely ; benzamide, *N*-methyl acetamide and *N*,*N*-dimethyl formamide in the frequency range of 0.1 to 100 kHz and in the varying temperature regions. A correlation of σ with the frequency has been made. An estimate of activation energy for conductivity has also been made.

Keywords : Relaxation time, conductivity, activation energy, polymer matrix.

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1. Introduction

NMR studies (Lowe 1968, Binsch 1968, Allan *et al* 1972) have shown the presence of restricted rotation about the C−N bond in amides. The barrier to internal rotation has generally been ascribed to the partial double bond character of the C−N bond of the amide group. It has been observed by Matsuo and Shosenji (1969) that internal rotation is strongly restricted at low temperatures. Comparatively high values for energy barriers to the internal rotation about formal single bonds have been observed in a number of molecules (Gutowsky and Holm 1956, Blears 1964, Anet and Ahmad 1964). Such high values of energy barrier is attributed to conjugated interaction between π electron on both sides of the single bond which induces restricted rotations of these groups.

Investigations on large number of amides using NMR by several workers yielded varying values for the energy barrier to the internal rotations. Binsch (1968) has made a comprehensive review of intramolecular process and has pointed out the existing disagreement in the energy barrier data reported by various workers using NMR. It has been suggested by earlier workers that the energy barrier of the C−N bond is influenced by steric hindrance, resonance and inductive effects.

In view of existing disagreement in the energy barrier data by NMR and that of very little effort persued to study rotational behaviour in amides using dielectric technique, it seemed important to utilize the dielectric absorption method to investigate the hindered rotations in amides. The dielectric method can determine a wide range of energy barriers provided the absorption peaks fall within the frequency range of the equipment for the available temperature region.

The polystyrene matrix method for studying the intramolecular processes has been found very useful in many cases as reported by Davies *et al* (Davies and Swain 1971, Davies and Edwards 1967) and later supported by Walker *et al* (Tay and Walker 1975, Tay *et al* 1976, McLellan and Walker 1977). The method which provides for the separation of the molecular and group processes in most of the systems, was therefore utilized for studying the energy barriers and other relaxation parameters of several amides by Chan *et al* (1983). The ΔH_ϵ values for the group process was found to lie in the range 52-75 kJ mol^{-1}. These measurements were extended to cover a cyclic system, benzamide for its dielectric behaviour.

Further, since the dielectric investigations account for the dispersion behaviour associated with molecular configuration and its ordering, which in turn affects the conductivity of the system, it was considered interesting to examine the AC conductivity of three such amides, namely, benzamide, N-methyl acetamide, N,N-dimethyl formamide using dielectric data. The dielectric data of the latter two species were taken from an earlier paper of Chan *et al* (1983). The molecules chosen were such that they represent the constituents from formamide to amide group substituted to benzene ring.

The present study therefore reports the dielectric and conductivity behaviour on the above systems in the frequency range of 0.1 to 100 kHz and at varying temperatures.

2. Experimental details

The dielectric measurements have been made on GR bridge in the frequency range of 0.1 to 100 kHz. The apparatus and measurement technique have been described by Tay and Walker (1975).

We have adopted the Davies and Swain (1971) procedures both experimentally and in the evaluation of the relaxation time and the distribution parameter by means of the Fuoss-Kirkwood equation. The polystyrene had a weight average molecular weight $\bar{M}_w$ of 230 000. The matrix solutions were prepared by dissolving weighed quantities of polystyrene and the desired solute in a non-polar solvent, trans 1,2-dichloro-ethylene, which was subsequently removed by heating to 360 K followed by treatment in a heated vacuum oven. The resultant matrix mass was pressed in a cylindrical die heated to 390 K to produce a sample disk 2.0 inch in

diameter and approximately 0.065 inch in thickness. Prior to pressing, the matrix mass containing the solute was returned to the vacuum oven at 360 K for 24 hours with no resultant weight loss, indicating that this preparation procedure did not produce any loss of solute from the matrix.

To obtain the relaxation time τ, Fuoss-Kirkwood equation (Fuoss and Kirkwood 1941) as given below was used.

$$\cos h^{-1}(\epsilon''_{max}/\epsilon'') = \beta \ln (f_{max}/f)$$

$$\tau = 1/2\pi f_m \tag{1}$$

where ϵ'', β, τ and f_m are dielectric loss, distribution function, relaxation time and frequency maxima respectively.

Analysis of relaxation time (τ) values as a function of temperature were carried out using Eyring relationship (Glasstone *et al* 1941) to yield ΔH_ϵ and ΔS_ϵ.

$$\log (\tau T) = \left(\frac{\Delta H_\epsilon}{R}\right)\left(\frac{1}{T}\right) - \left(\frac{\Delta S_\epsilon}{R} - \ln \frac{h}{k}\right) \tag{2}$$

A plot of log (τT) vs $\frac{1}{T}$ will give a straight line with slope equal to $\Delta H_\epsilon/R$ from which ΔH_ϵ can be calculated.

The value of free energy of activation ΔG_ϵ can be evaluated at various temperature using the following equation

$$\Delta G_\epsilon = RT \log \left(\frac{\tau k T}{h}\right) \tag{3}$$

Knowing the values of ΔH and ΔF, the ΔS is evaluated with the help of following equation

$$\Delta G_\epsilon = \Delta H_\epsilon - T.\Delta S_\epsilon \tag{4}$$

where ΔG_ϵ, ΔH_ϵ and ΔS_ϵ are the free energy, the enthalpy and the entropy of activation respectively. h, k and R are the plank's constant, boltzmann constant, and gas constant respectively.

The conductivity (σ) has been evaluated using the relation

$$\sigma = \epsilon_0 \epsilon'' \omega \tag{5}$$

where ϵ_0 is permittivity of free space.

3. Results

The results of Eyring rate equation analysis along with the relaxation times for benzamide are reported in Table 1. The conductivity data for benzamide, *N*-methyl acetamide and *N*,*N*-dimethyl formamide are given in Tables 2 and 3 respectively.

Table 1. Relaxation data and Eyring activation parameter for benzamide in a polystrene matrix.

Temperature (K)	$\tau \times 10^5$ sec	ΔG_ϵ kJ mol^{-1}	ΔH_ϵ kJ mol^{-1}	ΔS_ϵ J mol^{-1} deg^{-1}
162.3	17.9	27.3	31.2	24.2
164.3	14.9	27.4		23.2
177.8	2.6	27.2		22.5
184.6	1.1	26.9		23.0
192.8	0.5	26.9		22.4

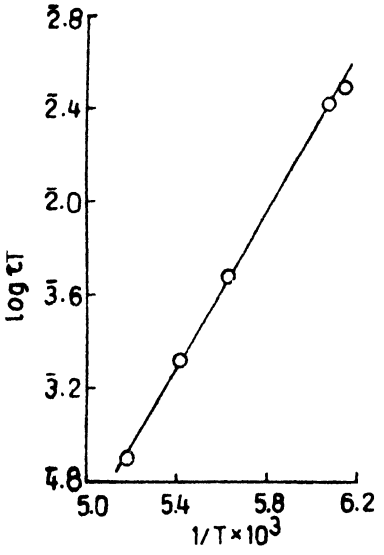
Table 2. Conductivity ($\sigma \times 10^{12}$) Ω^{-1} cm^{-1} of benzamide at frequencies.

Temperature (K)	0.1 kHz	0.2 kHz	1 kHz	2 kHz	5 kHz	10 kHz	20 kHz	50 kHz	100 kHz
162.3	2.79	5.79	15.0	30.24	143.2	275.2	526.9	1166.8	1892.2
164.3	-	6.47	16 68	33.69	162.7	314.9	609.2	1446.4	2600.0
177.8	-	6.46	17.31	35.70	183.1	366.4	720.7	1765.9	3326.0
184.6		6.48	17.20	36.08	191.2	-	773.7	1887.2	3762.2
192.8	-	6.26	16.86	35.88	196.2	407.1	826.9	2070.4	4054.7

Table 3. Conductivity ($\sigma \times 10^9$) Ω^{-1} cm^{-1} at frequencies.

Temperature (K)	0.2 kHz	0.5 kHz	1 kHz	2 kHz	5 kHz	10 kHz	20 kHz	50 kHz	100 kHz
				N-methyl acetamide					
299.6	1.26	3.32	6.63	12.85	31 15	-	115.5	267.8	--
303.4	1.25	3.27	6.60	12.90	31.23	-		268.1	507.5
307.5	1.15	3.16	6.57	-	31.40	60.82	117.8	270.6	508.0
310.4	1.10	3.10	6.47	12.95	31.60	61.13	118.3	270.8	508.5
312.5	1.06	3.02	6.36	12.81	31.64	55.64	118.1	268.9	-
316.0	1.00	2.92	6.24	12.79	28.91	-	119.6	271.3	509.3
319.0	0.95	2.79	6.07	12.48	31.60	62.10	119.7	271.5	509.7
328.0	0.82	2.44	5.49	11.78	30.90	61.70	121.9	274.4	—
332.0	0.76	2.26	5.13	11.20	30.40	61.10	120.2	274.8	—
				N,N-dimethyl formamide					
292.4	0.89	2.33	4.63	8.93	20.98	39.75	74.17	156.4	—
297.9	0.83	2.24	4.54	8.91	21.35	40.68	76.29	163.9	—
302.6	0.76	2.13	4.45	8.87	21.48	41.07	75.76	166.2	286.3
309.6	0.67	1.95	4.21	8.55	21.38	41.46	80.42	175.9	312.0
316.9	0.58	1.73	3.83	8.14	20.95	41.45	80.42	172.6	299.1
323.7	0.49	1.53	3.49	7.57	20.20	40.66	80.42	175.9	312·0
333.9	0.40	1.23	2.87	6.51	18.37	38.91	79.02	179.5	325.7

Figure 1 shows the plot of log τT versus $1/T$ for benzamide. The graphical representation of log σ versus log f for benzamide at 162.3 K and 164.3 K is given



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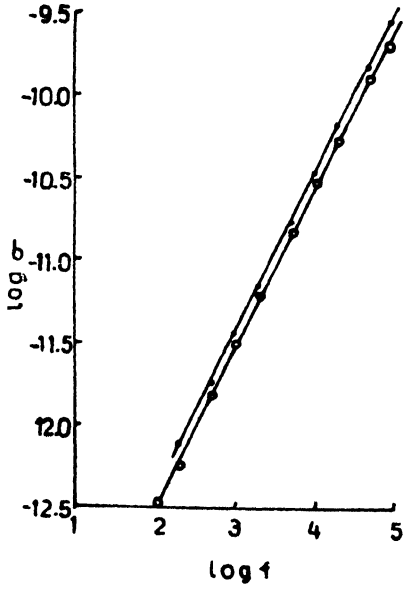

Figure 2. Log σ versus log f for benzamide. ● 164.3 K, ○ 162.3 K

in Figure 2. Figure 3 represents plot of log σ versus log f for *N*-methyl acetamide and *N,N*-dimethyl formamide. Figure 4 shows plot of log σ versus $1/T$ for benzamide, *N*-methyl acetamide and *N,N*-dimethyl formamide.

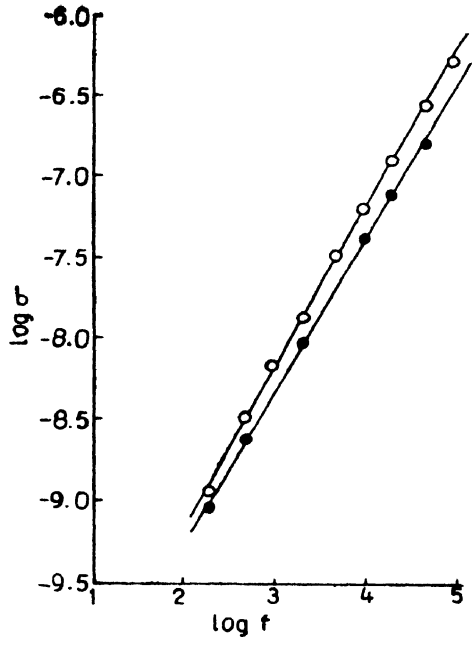

Figure 3. Log σ versus log f for *N*-methyl acetamide at 310 KO/ and *N,N*-dimethyl formamide. at 298 K ●

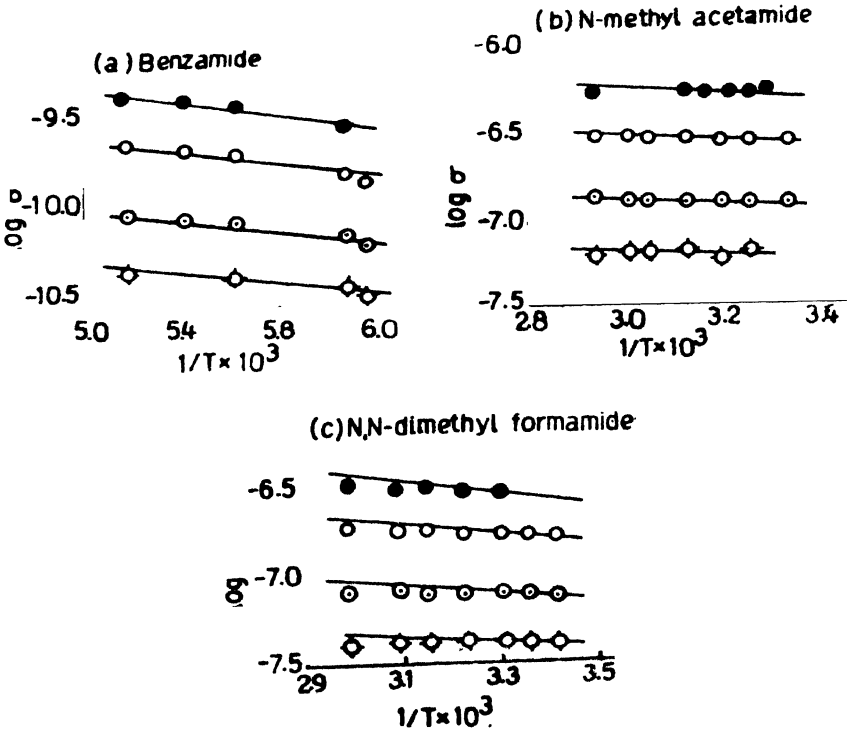

Figure 4. Log σ versus 1/*T*. ● 100 KHz, ○ 50 KHz, ⊙ 20 KHz, -Ȯ- 10 KHz

4. Discussion

4.1. Dielectric behaviour :

The absorption exhibited by a molecular system having both molecular and intramolecular processes may appear at different temperatures for a given frequency range. Amides could give rise to molecular relaxation process, group relaxation, a nitrogen inversion or a cooperative process. The intramolecular process is influenced by various factors such as steric hindrance, inductive effects and conjugation while the molecular process depends upon the shape and size of the molecule. A cooperative process is characterized by energy barrier which is appreciably higher compared with that of the molecular and intramolecular processes.

Benzamide examined in a polystyrene matrix gave rise to a single absorption peak in the temperature range of 162-193 K, yielding an enthalpy of activation ΔH_ϵ of 31.2 kJ mol^{-1}. The free energy of activation at 193 K ($\Delta G_{\epsilon\,193}$) has been found to be 26.9 kJ mol^{-1}. This value of ΔH_ϵ is compared with the ΔH_ϵ of 60 kJ mol^{-1} and 66 kJ mol^{-1} for the group rotation around C–N bond of molecules namely *N,N*-dimethyl formamide and *N,N*-dimethyl acetamide reported by Chan *et al* (1983). Thus the possibility of rotation of group around C–N bond is ruled out in view of higher enthalpy values. The cooperative phenomena in a system if present yields much higher enthalpy. Therefore, the process exhibited by benzamide appears to be due to the molecular rotation of the entire molecule. The ΔH_ϵ value of 31.2 kJ mol^{-1} and ΔG_ϵ at 193 K of 26.9 kJ mol^{-1} obtained here were therefore compared with ΔH_ϵ of 29 kJ mol^{-1} and ΔG_ϵ at 200 K of 30 kJ mol^{-1} for molecular process of almost a similar sized molecule benzyl iodide (Shukla *et al* 1980). For further strengthening our argument, the enthalpy obtained was also compared with the ΔH_ϵ of 29 kJ mol^{-1} again for the molecular process of benzyl chloride (Shukla *et al* 1980), which is almost of similar size and shape. Since these values of ΔH_ϵ and ΔS_ϵ are in close agreement with the values obtained for molecular process, it may be suggested that the dielectric absorption observed here in benzamide is due to molecular process. The enthalpy for the group rotation, which would be expected to be much higher in the range of 50-75 kJ mol^{-1} as observed earlier by Chan *et al* (1983) thus could not be detected, probably due to overlap of cooperative and group process falling in much higher range.

4.2. Conductivity behaviour :

The conductivity has been found to increase with frequency in all the three amides under investigation. A slight increase with temperature has been observed for benzamide in the lower frequency region, which enhances in the region of higher

frequency. In the case of N-methyl acetamide and N,N-dimethyl formamide, with the increase of temperature conductivity decreases slightly in the lower frequency region whereas it increases slightly in the higher frequency region. The decrease in conductivity can be explained due to increased scattering by thermally excited lattice vibrations. The change in conductivity with varying frequency at a fixed temperature has been remarkably high. Conductivity σ varies from $(31.15\text{-}30.37)\times 10^{-9}\ \Omega^{-1}\ cm^{-1}$ at 5 kHz in the temperature range of 299.6-332 K for N-methyl acetamide, while at a fixed temperature 310.4 K, σ varies from $1.10\times 10^{-9}\text{-}5.08\times 10^{-7}\ \Omega^{-1}\ cm^{-1}$ for the frequency change of 0.2-100 kHz. Similar results are obtained for N,N-dimethyl formamide. It has been observed that the σ values for benzamide in the temperature region 162-193 K vary from $(1.43\text{-}1.96)\times 10^{-11}\ \Omega^{-1}\ cm^{-1}$ at 5 kHz.

Analysis of conductivity data shows that log σ exhibits a linear behaviour with log f (Figures 2 and 3) for these amides. It is thus seen that conductivity depends on frequency as characterized by the relation of the type $\sigma = A(\omega)^S$, where A and S are frequency independent constants. S has been found to vary from 0.95-1.0 in the temperature range 162-193 K for benzamide, 0.97-1.0 for N-methyl acetamide in the temperature range 299.6-320.0 K and, for N,N-dimethyl formamide from 0.94 to 1.0 in the temperature range 292.4-333.9 K. The values of S exhibit only slight change with temperature. This may be due to a small range of temperature variation observed for dispersion in the present systems.

The activation energy for the conductivity process has been evaluated using the relation of the type $\sigma = Ae^{-\Delta E/kT}$, where A is a constant and k is the Boltzmann's constant. From a linear plot of log σ vs $1/T$ (Figure 4) the activation energy (ΔE) obtained was found to be in the range of .025-.039 eV, .022-.033 eV and .037-.066 eV for the frequency range of 10-100 kHz for benzamide, N-methyl acetamide and N,N-dimethyl formamide respectively. No substantial change in the activation energy has been observed for the amides investigated here.

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